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NMR study of the ferroelastic-to-paraelastic protonic superionic transition in $Rb_3H(SeO_4)_2$

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The drastic changes in the angular dependence of the ^{87}Rb quadrupole-perturbed $\frac{1}{2}\rightarrow-\frac{1}{2}$ NMR spectra on going through $T_c=446$ K as well as the temperature dependence of the proton spectra demonstrate that the structural phase transition in $Rb_3H(SeO_4)_2$ involves a breakup of the SeO_4—$H\cdots SeO_4$ hydrogen-bonded dimers and the formation of a dynamic two-dimensional H-bonded network formed by reorienting $HSeO_4$ groups in the *a-b* plane. The temperature dependence of the order parameter, which measures the difference in the probabilities of H-bond formation in the three possible directions of the triangular lattice, has been deduced from the NMR spectra. The spin-lattice relaxation time measurements further allowed for a determination of the activation energy $E_a=0.45\pm0.05$ eV for defect formation, leading to proton conductivity even below T_c.

I. INTRODUCTION

$Rb_3H(SeO_4)_2$ is known to undergo[1,2] a structural phase transition at $T_c\approx446$K from a low-temperature ferroelastic[2] to a high-temperature paraelastic phase that exhibits protonic superionic conductivity.[2] The primitive unit cell of the low-temperature, ferroelastic phase is monoclinic with $z=2$ and space group[1] $A2/a$, whereas the high-temperature primitive cell is rhombohedral with $z=1$ and space group $R\bar{3}m$.[2] The instability leading to the structural phase transition occurs in the F point of the Brillouin zone of the rhombohedral cell[2] and is connected with a doubling of the unit-cell volume. Since the small representation of the wave vector **k** of the soft mode is one-dimensional and the star of **k** contains three arms, the structural phase transition must be described[2] by a three-component order parameter.

The basic elements of the structure of the low-temperature phase[1,2] are groups of two SeO_4 tetrahedra, which are tilted towards each other and are connected with an O(2)—H $\cdots$ O(2′) hydrogen bond. The length of this bond is 2.51 Å and the proton seems to be dynamically disordered between two equivalent equilibrium sites. We may thus say that the low-temperature structure consists of H-bonded SeO_4 dimers. The structure is very open since there are three possible dimeric configurations, i.e., three possible O—H $\cdots$ O bonds and corresponding $HSeO_4$ orientations out of which only one is realized in a given ferroelastic domain of the low-temperature phase.

It seems possible that at the transition to the high-temperature phase the dimeric structure is breaking up and that the $HSeO_4$ groups start to reorient between the three equilibrium orientations. This leads to the formation of a dynamic two-dimensional O—H $\cdots$ O bonded network of SeO_4 groups where each O—H $\cdots$ O bond is realized with a probability $\frac{1}{3}$.

To throw some further light on this hypothetical model, which is based on the x-ray data,[2] we decided to perform a ^{87}Rb and proton NMR study of the ferroelastic phase transition in $Rb_3H(SeO_4)_2$. We particularly hoped to see the effects of $HSeO_4$ rotation and the formation of the time-dependent dynamic O—H $\cdots$ O bond network on the ^{87}Rb NMR spectra and spin-lattice relaxation rate T_1^{-1}.

II. THE ORDER PARAMETER AND LANDAU THEORY

To understand the NMR experiments, let us first introduce the order parameter describing the transition from the dimeric structure of the low-temperature phase to the dynamic two-dimensional H-bonded network of the high-temperature phase.

As already mentioned, there are three possible O—H $\cdots$ O bonds—designated 1, 2, and 3—connecting a given SeO_4 group with its three nearest neighbors. The directions of these O—H $\cdots$ O bonds form a triangular lattice in the *a-b* plane (Fig. 1).

Let us now designate the probability that one of these three O—H $\cdots$ O bonds is formed by n_i $(i=1,2,3)$. On the time average we have

$$\langle n_1\rangle+\langle n_2\rangle+\langle n_3\rangle=1\ . \tag{1}$$

For $T>T_c$ all three bonds are equivalent on the time average and each is realized with a probability $\frac{1}{3}$:

$$\langle n_1\rangle=\langle n_2\rangle=\langle n_3\rangle=\tfrac{1}{3},\quad T>T_c\ . \tag{2}$$

Below T_c, on the other hand, only one set of H bonds is realized in a given domain so that, e.g.,

$$\langle n_1\rangle=1,\quad \langle n_2\rangle=\langle n_3\rangle=0,\ \text{etc.},\quad T<T_c\ . \tag{3}$$

The H-bond order parameter can be now introduced as

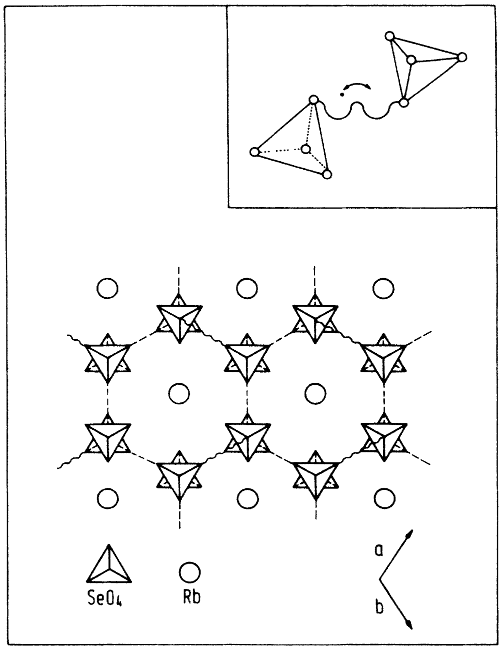

FIG. 1. Projection of the H-bond network formed above T_c by reorienting $HSeO_4$ groups on the *a*-*b* plane. The wavy line shows the direction of the given O(2) · · · O(2) H bond, while the dotted lines represent the two other possible O(2) · · · O(2) H-bond directions in the *a*-*b* plane. The dimeric structure of the low-temperature phase is shown in the inset.

$$\xi_i = \langle n_i \rangle - \tfrac{1}{3}, \quad i = 1,2,3 \; . \tag{4}$$

It is zero above T_c, whereas at least one component is nonzero below T_c.

The H-bond part of the free energy can be now expanded in terms of the order-parameter components:

$$\begin{aligned} F(T,\xi_1,\xi_2,\xi_3) = {} & F_0 + A(\xi_1^2+\xi_2^2+\xi_3^2) + B(\xi_1^4+\xi_2^4+\xi_3^4) \\ & + C[\xi_1^2(\xi_2^2+\xi_3^2)+\xi_2^2\xi_3^2] \\ & + D(\xi_1^6+\xi_2^6+\xi_3^6) + \cdots \; . \end{aligned} \tag{5}$$

Here $A = \alpha(T - T_c)$ is temperature dependent, whereas *B*, *C*, *D* are positive constants. The cubic term is forbidden due to symmetry reasons. The temperature dependence of the order parameter is now obtained from the equilibrium conditions:

$$\left[\frac{\partial F}{\partial \xi_1} \right]_{\xi_{10},\xi_{20},\xi_{30}} = \left[\frac{\partial F}{\partial \xi_2} \right]_{\xi_{10},\xi_{20},\xi_{30}} = \left[\frac{\partial F}{\partial \xi_3} \right]_{\xi_{10},\xi_{20},\xi_{30}} = 0 \; . \tag{6}$$

For $T > T_c$, $\xi_{i0} = 0$, whereas for $T < T_c$ we get three different domains: (a) $\xi_{10} \neq 0$, $\xi_{20} = \xi_{30} = 0$, (b) $\xi_{20} \neq 0$, $\xi_{10} = \xi_{30} = 0$, and (c) $\xi_{30} \neq 0$, $\xi_{10} = \xi_{20} = 0$.

The total free energy is a sum of an H-bond part, an elastic part and an H-bond-elastic strain coupling term.[3] For NMR, the H-bond part is crucial. Because of that only this part is treated here. The elastic part renormalizes the quadratic terms and changes the sign of the constant *B*, which becomes negative. Thus the phase transition becomes a first-order one.

III. EXPERIMENTAL

The ^{87}Rb NMR spectra and spin-lattice relaxation times have been studied on a single crystal of $Rb_3H(SeO_4)_2$ at a Larmor frequency $(\omega_L/2\pi) = 88.411$ MHz, whereas the proton NMR measurements were performed at 269.958 MHz. The spin-lattice relaxation time (T_1^{-1}) data were checked for a possible Larmor frequency dependence at 27.99 MHz for ^{87}Rb and at 88.41 and 60.47 MHz for protons. Pulsed Fourier transform NMR was used in all measurements.

IV. THEORY

The electric-field gradient (EFG) tensor at a given ^{87}Rb site depends on the $HSeO_4$ orientations. The quadrupole perturbed NMR frequency of a Rb nucleus at site *l* can be thus expanded in powers of the order-parameter components ξ_{i0}. Up to first-order terms we find

$$\nu_l = \nu_{l,0} + \sum_{m \neq l} \sum_{i=1}^{3} a_{ml,i} \xi_{i0,m} + \cdots \; . \tag{7a}$$

Here the sum over *m* goes over all neighboring $HSeO_4$ groups and the coefficients $a_{ml,i}$ depend on the distance between the lattice points *l* and *m* as well as on the orientation of the external magnetic field with respect to the crystal axes.

The temperature dependence of the quadrupole shift of the NMR frequency thus reflects the temperature dependence of the equilibrium order-parameter components ξ_{i0}.

Although the relation between the ^{87}Rb quadrupole coupling and the order parameter is nonlocal, it is definitely local for the case of proton chemical shift tensor interactions. Here

$$\nu_l = \nu_{l,0} + C_i \xi_{i,0,l}, \quad i = 1,\ 2,\ \text{or}\ 3 \; . \tag{7b}$$

The ^{87}Rb spin-lattice relaxation rate, T_1^{-1}, on the other hand, is expected to measure the local spectral density $J(\omega)$ of the fluctuations in the quadrupole coupling, which are related to the order-parameter fluctuations.

The instantaneous value of the order parameter ξ_i can be divided into a time averaged, static part ξ_{i0} and a time-dependent part $\delta\xi_i(t)$:

$$\xi_i = \xi_{i0} + \delta\xi_i(t) \; , \tag{8}$$

where

$$\langle \xi_i \rangle = \begin{cases} \xi_{i0} = 0, & T > T_c \; , \quad (9a) \\ \xi_{i0} \neq 0, & T < T_c \quad (9b) \end{cases}$$

and where

$$\langle \delta\xi_i(t) \rangle = 0, \quad \langle \delta\xi_i^2(t) \rangle \neq 0 \; , \tag{9c}$$

both above and below T_c. Introducing collective coordinates $\delta\xi_{i,q}$ via the Fourier transform of $\delta\xi_{i,m}$, one finds in the random-phase approximation,

$$\frac{1}{T_1} \propto J(\omega) \propto \sum_{q}\sum_{i}\int_{-\infty}^{+\infty}\langle \delta\xi_{i,q}(0)\delta\xi_{i,-q}(t)\rangle e^{-i\omega t}dt \ , \tag{10}$$

where the sum over q goes over the soft-mode branch.

Using the fluctuation-dissipation theorem we finally find

$$\frac{1}{T_1} \propto \sum_{q}\chi''(q,\omega) \ ,$$

where $\chi''(q,\omega)$ is the imaginary part of the wave-number-dependent generalized dynamic order-parameter susceptibility and the sum over q again runs over the soft-mode branch. Since $\chi''(q,\omega)$ shows[2] a peak at T_c, one expects a dip in T_1 as $T \rightarrow T_c$ if the soft-mode fluctuations represent the main relaxation mechanism. Still another possible relaxation mechanism is relaxation via thermally activated diffusing defects leading to protonic conductivity even below T_c.

V. RESULTS AND DISCUSSION

The temperature dependence of the ^{87}Rb $\frac{1}{2} \rightarrow -\frac{1}{2}$ quadrupole perturbed NMR transitions is shown in Fig. 2 for an orientation where the three-fold axis of the high-temperature phase is perpendicular to the external magnetic field: $\mathbf{c} \perp \mathbf{H}_0$, $\theta \sphericalangle \mathbf{a},\mathbf{H}_0 = 22.5°$. The eleven sharp low-temperature ^{87}Rb lines collapse at T_c into two broad lines characteristic for the two inequivalent Rb sites of the high-temperature primitive cell. The phase transition is rather sharp demonstrating that it is close to a first-order one. The shape of the spectra below and above T_c are shown in Fig. 3. The coexistence of sharp and broad lines at the phase transition is another evidence for the I order nature of this phase transition (Fig. 2).

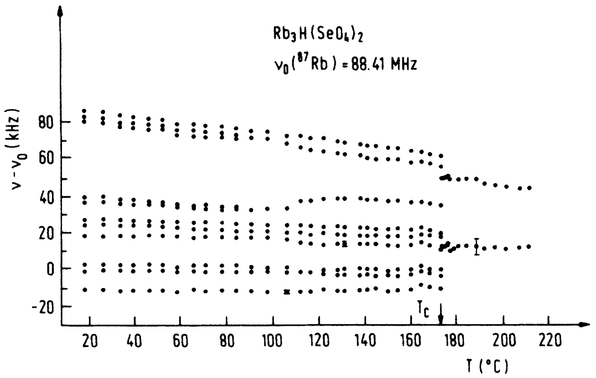

FIG. 2. Temperature dependence of the ^{87}Rb $\frac{1}{2} \rightarrow -\frac{1}{2}$ transition frequencies for $\mathbf{c} \perp \mathbf{H}_0$, $\theta = \sphericalangle(a,H_0) = 22.5°$.

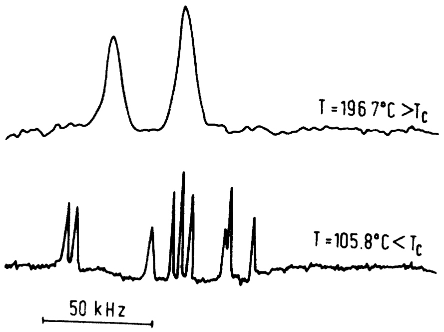

FIG. 3. ^{87}Rb $\frac{1}{2} \rightarrow -\frac{1}{2}$ NMR line shapes below and above T_c.

The angular dependence of the NMR transition frequencies is shown in Fig. 4(a) for the $\mathbf{c} \perp \mathbf{H}_0$ rotation at $T = 293$ K $< T_c$. The spectra are strongly anisotropic. Since there are six Rb sites per perimitive cell for $T < T_c$ and we see a maximum of eleven anisotropic lines, we obviously deal with different ferroelastic domains. Above T_c the spectra become at this orientation ($\mathbf{c} \perp \mathbf{H}_0$) practically isotropic [Fig. 4(b)]. This is indeed expected for the case of fast reorientations of the HSeO$_4$ groups around the c axis while forming a two-dimensional dynamic O—H $\cdots$ O bond network parallel to the a-b plane. If $\mathbf{H}_0$ is not perpendicular to the c axis, the ^{87}Rb spectra are anisotropic even above T_c as expected [Fig. 4(c)].

The drastic change in the angular dependence of the ^{87}Rb spectra at T_c for $\mathbf{c} \perp \mathbf{H}_0$ as well as the disappearance of the ferroelastic domain structure and the reduction in the number of inequivalent Rb sites on going through T_c

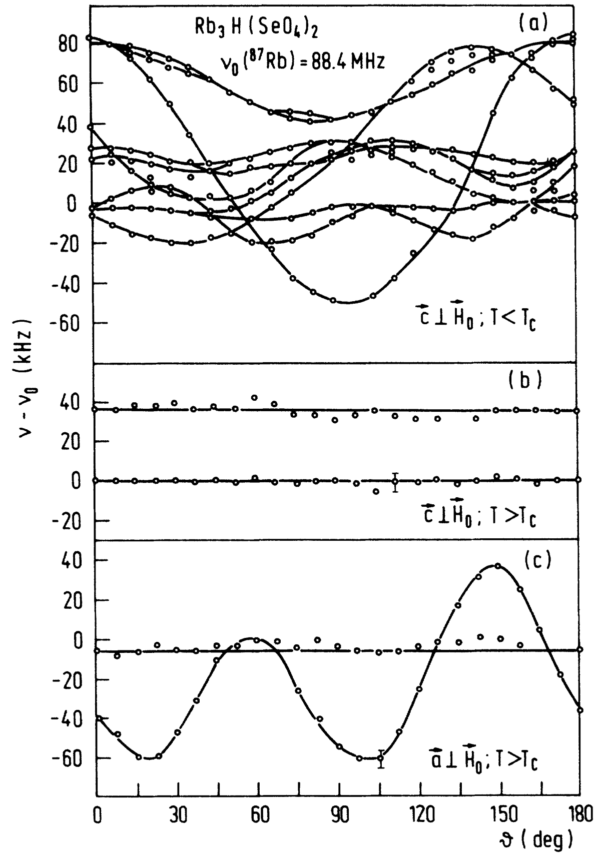

FIG. 4. Angular dependence of the ^{87}Rb $\frac{1}{2} \rightarrow -\frac{1}{2}$ NMR spectra: (a) $T < T_c$, $\mathbf{c} \perp \mathbf{H}_0$, $\theta \sphericalangle (\mathbf{a},\mathbf{H}_0)$; (b) $T > T_c$, $\mathbf{c} \perp \mathbf{H}_0$, $\theta \sphericalangle (\mathbf{a},\mathbf{H}_0)$; (c) $T > T_c$, $\mathbf{a} \perp \mathbf{H}_0$, $\theta \sphericalangle (\mathbf{c},\mathbf{H}_0)$.

thus indeed support the proposed phase transition model involving a change from H-bonded SeO_4 dimers below T_c where $\xi_{i0} \neq 0$ to a dynamic two-dimensional O—H $\cdots$ O bonded network formed by reorienting $HSeO_4$ groups above T_c where $\xi_{i0}=0$. The same is true for the proton spectra. The proton spectrum taken at $\nu_0(^1H)=270$ MHz for $c \perp H_0$ is a doublet, $\Delta\nu \approx 7$ kHz≈ 25 ppm for $T<T_c$, which collapses into a singlet for $T>T_c$ where $\xi_{i0}=0$.

We believe that the above splitting is due to the anisotropy of proton chemical shift tensor and can be described by expression (7b). The temperature dependence of this splitting, which is rather similar to the one observed in the ^{87}Rb spectra, and the associated temperature dependence of the order parameter ξ_{i0} are shown in Fig. 5.

The temperature dependence of the ^{87}Rb spin-lattice relaxation time is shown in Fig. 6. T_1 is independent of the Larmor frequency between 29 and 88 MHz, is thermally activated with $E_a=0.45 \pm 0.05$ eV and strongly *decreases* with increasing temperature between 273 and 500 K without showing a pronounced anomaly at T_c. It changes from ≈ 60 ms at room temperature to less than 0.8 ms for $T \geq T_c$. The temperature dependence of T_1 is thus very different from the one expected for relaxation via soft-mode fluctuations [Eq. (10)] where a pronounced dip in T_1 is usually found at T_c. A similar thermally activated temperature dependence of T_1 with $E_a=0.45 \pm 0.05$ eV is also observed in the proton data at 270, 60.47, and 88.41 MHz. Here too T_1 is independent of the Larmor frequency.

The activation energy $E_a \approx 0.45$ eV, which determines the T dependence of T_1, is rather close to the one[2] found to determine the temperature dependence of the protonic conductivity.[2] We therefore believe that both the ^{87}Rb and the proton spin-lattice relaxation rates are governed by the creation of H_2SeO_4 or SeO_4 defects, i.e., broken O—H $\cdots$ O bonds and rotated SeO_4 groups, responsible for the onset of protonic conductivity even below T_c.

In such a case we deal with random motions; T_1 can be, as usual, described by Bloembergen-Purcell-Pound (BPP) equation:[4]

$$\frac{1}{T_1}=K^2\frac{\tau_c}{1+\omega_L^2\tau_c^2}\ , \tag{11a}$$

where $\tau_c=\tau_0\exp(E_a/kT)$ is the correlation time and K^2 measures the mean-squared fluctuation in the ^{87}Rb quadrupole coupling due to the motion of defects. Since T_1 is independent of the Larmor frequency ω_L we are obviously in the fast motion regime $\omega_L\tau \ll 1$, so that one expects that

$$T_1^{-1}=K^2\tau_0\exp(E_a/kT) \tag{11b}$$

and $T_1 \propto e^{-E_a/kT}$ should increase with increasing temperature. In fact T_1 *decreases* with increasing temperature. This can be understood if the defect motion is not random but strongly biased. In such a case expression (11a) is changed[5] to

$$\frac{1}{T_1}=K^2\frac{\tau}{1+\omega_L^2\tau^2}\frac{4a}{(1+a)^2}\ , \tag{12a}$$

where $a=e^{\Delta U/kT}$ and $\Delta U=E_2-E_1$ measures the difference in energy between the ground state and the excited defect state (see inset to Fig. 6). Here

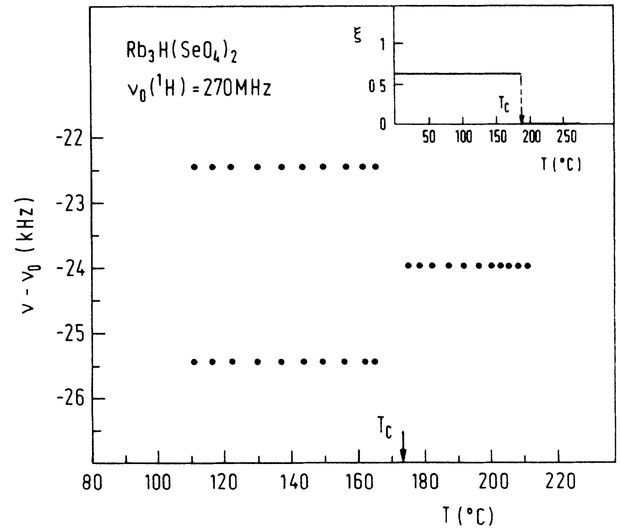

FIG. 5. Temperature dependence of the proton doublet splitting for $H \perp c_0$. Inset shows the temperature dependence of the order parameter of the transition ξ_{i0} measuring the difference in the probabilities of H-bond formation along the three possible directions determined by the $HSeO_4$ orientations in the triangular lattice.

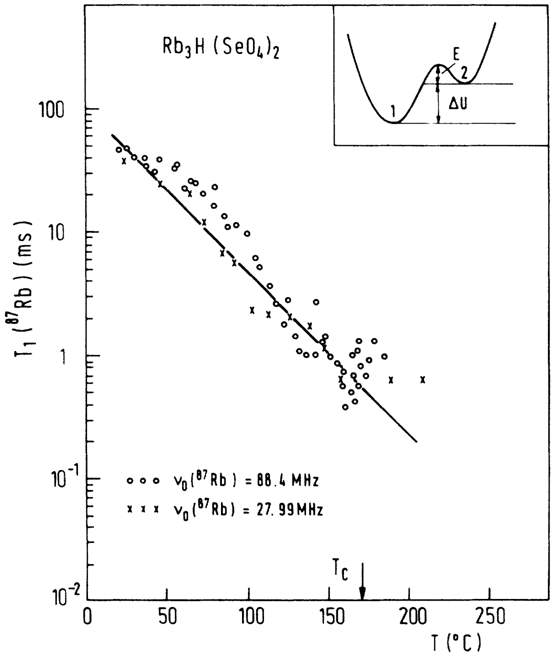

FIG. 6. Temperature dependence of the ^{87}Rb spin-lattice relaxation time T_1. The inset shows the asymmetric double minimum potential for defect formation.

$$\frac{1}{\tau}=\frac{1}{\tau_+}+\frac{1}{\tau_-}\approx\frac{1}{\tau_+} \tag{12b}$$

is the sum of the jump rates from the excited to the ground state ($1/\tau_+$) and from the ground state to the excited state ($1/\tau_-$). As $a \gg 1$ we find for $\omega_L \tau \ll 1$,

$$\frac{1}{T_1}=K^2 4\tau_0 e^{-(\Delta U-E)/kT} , \tag{12c}$$

where (Fig. 6) $\tau_+=\tau_0\exp(E/kT)$ and E is the height of the intervening potential barrier between the excited and the ground state as seen from the excited state. Since $\Delta U \gg E$ we see that T_1 must decrease with increasing temperature as indeed observed, $T_1 \propto e^{(\Delta U-E)/kT)}$, in spite of the fact that we are in the fast motion regime.

It should be stressed that protonic[6] conductivity below T_c requires two consecutive steps: the rotation of the $HSeO_4$ group connected with the breaking of the SeO_4-H-SeO_4 bond and the transfer of the proton from one site in the O—H $\cdots$ O bond to the other. We believe that the rate determining step is the rotation of the $HSeO_4$ group and that the observed activation energy $\Delta U - E = E_a = 0.45$ eV describes this process. The extremely short value of the observed ^{87}Rb T_1 and the associated large value of K^2, which practically coincides with the change in the ^{87}Rb quadrupole coupling on going through T_c, provide further support for this model.

We may thus conclude that both the ^{87}Rb and ^{1}H spectra, as well as the corresponding spin-lattice relaxation rates, provides additional microscopic evidence that the paraelastic-ferroelastic phase transition in $Rb_3H(SeO_4)_2$ at $T_c = 446$ K is connected with the breaking up of the dimeric SeO_4-H-SeO_4 structure of the low-temperature phase and the formation of the dynamic two-dimensional O—H $\cdots$ O bonded network of rotating $HSeO_4$ groups above T_c where each of the three possible O—H $\cdots$ O bonds is formed for $\frac{1}{3}$ of the time:

$$\frac{\tau_i}{\tau_1+\tau_2+\tau_3}=\tfrac{1}{3},\quad i=1,2,3 . \tag{13}$$

The NMR data further allow for the determination of the temperature dependence of the order parameter ξ_{i0} of the transition, as well as for the determination of the activation energy for defect formation leading to proton conductivity even below T_c.

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